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(54) **Organic fluorine compounds and curable compositions containing them**

Organische Fluorverbindungen und diese enthaltende vernetzbare Zusammensetzungen

Composés organiques fluorés et compositions réticulables les contenant

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## Description

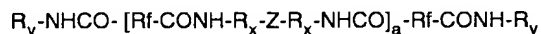
[0001] This invention relates to organic fluorine compounds which are useful as stock materials for rubber materials having solvent and chemical resistance and release agents. It also relates to curable compositions which e.g. when allowed to stand at room temperature or heated, will readily cure into cured products having good solvent, chemical and heat resistance.

## BACKGROUND

[0002] Organic fluorine compounds have been used in a variety of fields. For example, polymers of organic fluorine compounds are crosslinked with crosslinking agents to form elastomers which are utilized as rubber materials and mold release agents. Most elastomers obtained from conventional organic fluorine compounds, however, are less resistant to solvents and chemicals. There is a need for elastomers having higher solvent and chemical resistance.

[0003] Elastomers used as sealants and molded parts are desired to exhibit better mold release and water repellent properties.

[0004] Our EP/A/573283 describes fluorine-containing organopolysiloxane compositions which are room-temperature curable to solvent-resistant elastomers, based on organic fluorine compounds of the general formula

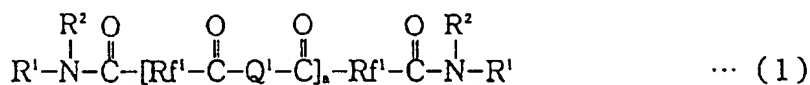


in which a is an integer which may be 0, Rf is a divalent perfluoroalkylene or perfluoropolyether group, R<sub>x</sub> is divalent hydrocarbon, R<sub>y</sub> is monovalent aliphatic unsaturated hydrocarbon and Z is a divalent siloxane group. The compositions are addition-cured by hydrogenorganopolysiloxane and platinum-family catalyst.

[0005] An object of the present invention is to provide a novel and useful organic fluorine compound which will form an elastomer having good solvent resistance, chemical resistance, mold release properties, and water repellency.

[0006] Another object of the present invention is to provide a curable composition based on a fluorinated amide compound and a fluorinated organohydrogensiloxane which will cure into a cured product having good solvent resistance, chemical resistance, mold release properties, and water repellency.

[0007] A first aspect of the present invention is an organic fluorine compound of the following general formula (1).

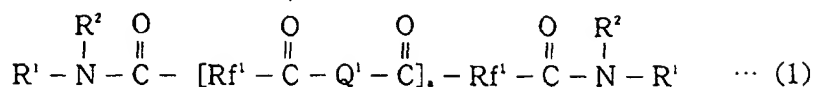
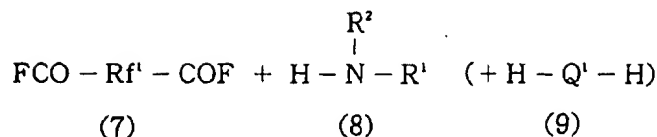


[0008] Groups R<sup>1</sup> are selected from halogen-substituted and unsubstituted monovalent C<sub>2-10</sub> alkenyl, cycloalkyl or alkenyl-substituted aryl groups. R<sup>2</sup> groups are selected from halogen substituted and unsubstituted mono-valent hydrocarbon groups Q<sup>1</sup> is a group represented by the following general formula (3):



wherein R<sup>4</sup> and R<sup>5</sup> are independently selected from halogen-substituted and unsubstituted divalent hydrocarbon groups. Rf<sup>1</sup> is a divalent perfluoroalkylene or perfluoropolyether group. Letter a is an integer which may be 0.

[0009] A second aspect of the invention is a method in which organic fluorine compound of formula (1) is obtained by reacting a compound having an acid fluoride group at either end of the following general formula (7) with a secondary amine compound of the following general formula (8) and optionally a compound of the following general formula (9) in the presence of an acid acceptor.



[0010] We have found that this organic fluorine compound can be converted into an elastomer having a high fluorine content and low surface energy.

[0011] A third aspect of the present invention provides a curable composition comprising (A) organic fluorine compound represented by formula (1) as defined above, (B) a fluorinated organohydrogensiloxane containing at least one monovalent perfluoroalkyl ether or perfluoroalkyl group and at least two hydrosilyl groups in a molecule, and (C) a platinum group catalyst. Component (B) is present in an amount to give 0.5 to 5 mol of the hydrosilyl group per mol of the unsaturated group in the composition.

[0012] We have found that when a compound represented by formula (1) is blended with a fluorinated organohydrogensiloxane as a crosslinking agent or chain extending agent and further with a platinum group catalyst, the resulting curable composition readily cures at room temperature into cured products having improved solvent resistance, chemical resistance and heat resistance.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is an IR spectrum chart of an organic fluorine compound prepared in Example 1.

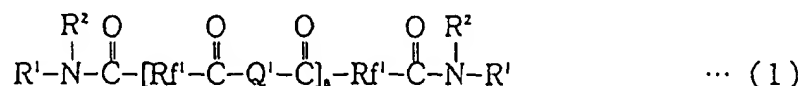
FIG. 2 is an IR spectrum chart of an organic fluorine compound prepared in Example 2.

FIG. 3 is an IR spectrum chart of an organic fluorine compound prepared in Example 3.

FIG. 4 is an IR spectrum chart of an organic fluorine compound prepared in Example 4.

#### FURTHER EXPLANATIONS; PREFERRED AND OPTIONAL FEATURES

[0014] The organic fluorine compounds proposed herein are represented by the general formula (1).



[0015]  $\text{R}^2$  in formula (1) are independently selected from substituted or unsubstituted monovalent hydrocarbon groups, preferably having 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, for example, alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, nonyl and decyl; cycloalkyl groups such as cyclopentyl, cyclohexyl, and cycloheptyl; alkenyl groups such as vinyl, allyl, propenyl, isopropenyl, butenyl, isobutenyl, hexenyl, and cyclohexenyl; aryl groups such as phenyl, tolyl, xylyl, and naphthyl; aralkyl groups such as benzyl, phenylethyl, and phenylpropyl; and substituted ones of these groups wherein some or all of the hydrogen atoms are replaced by halogen atoms including fluorine, chlorine and bromine, such as chloromethyl, bromoethyl, chloropropyl, and trifluoropropyl.

[0016]  $\text{R}^1$  in formula (1) is a halogen substituted and unsubstituted monovalent hydrocarbon group of 2 to 10 carbon atoms, especially up to 8 carbon atoms selected from an alkenyl group such as vinyl, allyl, propenyl, isopropenyl, butenyl, isobutenyl, hexenyl; a cycloalkenyl group such as cyclohexenyl; and an alkenyl-substituted aryl group such as styryl.

[0017] Note: R<sup>1</sup>'s and R<sup>2</sup>'s at opposite ends of the molecule may be but need not be the same.

[0018] Q<sup>1</sup> in formula (1) is a group represented by the following general formula (3).



[0019] R<sup>4</sup> and R<sup>5</sup> in formula (3) are independently selected from unsubstituted divalent hydrocarbon groups, preferably having 1 to 10 carbon atoms, more preferably 2 to 6 carbon atoms, for example, alkylene groups such as methylene, ethylene, propylene, methylethylene, butylene, and hexamethylene, cycloalkylene groups such as cyclohexylene and substituted ones of these groups wherein some or all of the hydrogen atoms are replaced by halogen atoms.

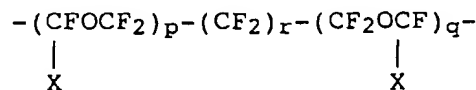
[0020] Examples of the group of formula (3) represented by Q<sup>1</sup> in formula (1) are given below. Note that in the following chemical formulae, Me is methyl and Ph is phenyl.



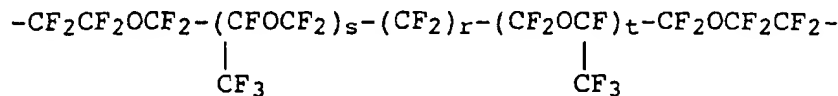
[0021] In formula (1), Rf<sup>1</sup> is a divalent perfluoroalkylene or perfluoropolyether group. The divalent perfluoroalkylene group is preferably represented by the formula:



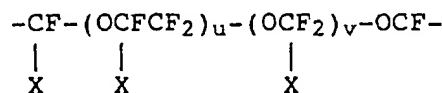
wherein m = 1 to 10, preferably 1 to 6. The divalent perfluoropolyether group is preferably represented by the following formulae:



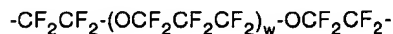
wherein X is F or CF<sub>3</sub> group, p, q and r are integers in the range: p ≥ 1, q ≥ 1, and 2 ≤ p + q ≤ 200, especially 3 ≤ p + q ≤ 110 and 0 ≤ r ≤ 6,



wherein r, s and t are integers in the range: 0 ≤ r ≤ 6, s ≥ 0, t ≥ 0, and 2 ≤ s + t ≤ 200, especially 3 ≤ s + t ≤ 110,

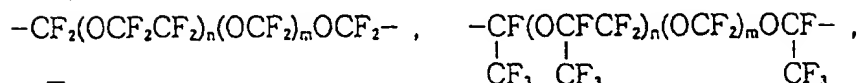
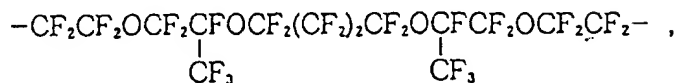
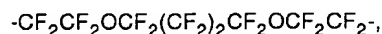
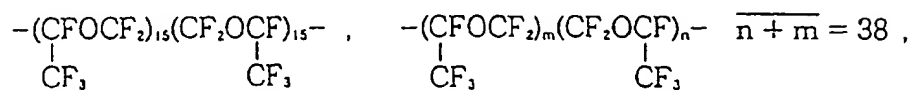
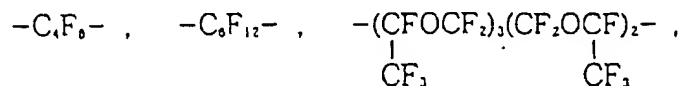


wherein X is F or CF<sub>3</sub> group, u and v are integers in the range: 1 ≤ u ≤ 20 and 1 ≤ v ≤ 20, and



wherein w is an integer in the range: 1 ≤ w ≤ 20.

[0022] Examples of Rf<sup>1</sup> are given below.

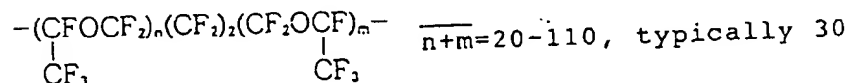
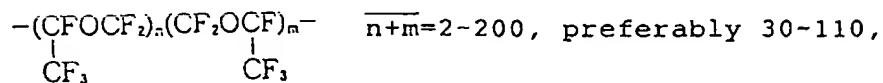
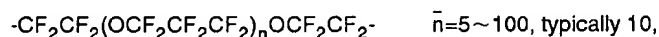


$\overline{n}=5-50$ , typically 8

$\overline{m}=1-10$ , typically 2

$\overline{n}=5-50$ , typically 15

$\overline{m}=1-10$ , typically 2

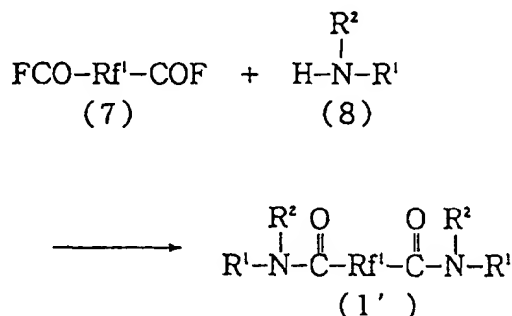


[0023] In formula (1), letter a is an integer and may be 0. The organic fluorine compound of formula (1) contains at least one divalent perfluoroalkylene or perfluoropolyether group while letter a is preferably an integer of 0 to 10, more

preferably equal to 0, 1, 2, 3, 4, 5 or 6.

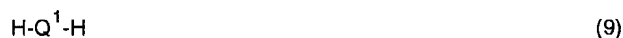
[0024] The organic fluorine compounds of formula (1) may exist and be used in various forms, from low viscosity polymers having a viscosity of several tens of centistokes at 25°C to solid raw rubber-like polymers. For ease of handling, raw rubber-like polymers are preferred for the intended application as heat vulcanizable rubber and polymers having a viscosity of  $10^{-4}$  to  $10^{-1}$  m<sup>2</sup>s<sup>-1</sup> (100 to about 100,000 centistokes) at 25°C are preferred for the intended application as liquid rubber. Too low viscosity would be undesirable because cured products would have low elongation as elastomers and imbalance of physical properties.

[0025] The organic fluorine compounds or fluorinated amide compounds of formula (1) may be obtained by the following method. The fluorinated amide compound of formula (1) wherein letter a is equal to 0 can be synthesized by reacting a compound having an acid fluoride group at either end of the following general formula (7) with a secondary amine compound of the following general formula (8) in the presence of an acid acceptor such as trimethylamine.



[0026] Note that R<sup>1</sup>, R<sup>2</sup> and R<sup>f</sup> are as defined previously.

[0027] Also the fluorinated amide compound of formula (1) wherein letter a is an integer of at least 1 can be synthesized by reacting a compound having an acid fluoride group at either end of formula (7) with a compound having an amino group at either end of the following general formula (9):



wherein Q<sup>1</sup> is as defined previously in the presence of an acid acceptor and further reacting with a secondary amine compound of formula (8).

[0028] Although the compound having an acid fluoride group at either end of formula (7) and the secondary amine compound of formula (8) may be used in any desired ratio, it is preferred that the molar ratio of the charge (a) of the formula (7) compound to the charge (b) of the formula (8) compound, (a)/(b), range from 0.5 mol/mol to 2 mol/mol.

[0029] Also the compound of formula (7) and the compound of formula (9) are mixed such that the molar charge (a) of the formula (7) compound is not less than the molar charge (c) of the formula (9) compound. The number (represented by a) of recurring units in formula (1) may be controlled to an appropriate value by adjusting the molar ratio (a)/(c). Higher values of (a)/(c) allow for synthesis of polymers having a relatively low molecular weight whereas molar ratios (a)/(c) approximating to 1 allow for synthesis of polymers having a high molecular weight.

[0030] Reaction conditions are not critical. Preferred conditions include a temperature of 20 to 100°C and a time of about 1 to 8 hours, more preferably a temperature of 20 to 50°C and a time of about 2 to 4 hours.

[0031] Preferably the reaction is effected at about 50 to 150°C, especially about 80 to 120°C, for about 2 to 4 hours.

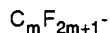
[0032] The organic fluorine compounds of the present invention can form elastomers having a high fluorine content and low surface energy, which will find use in a variety of applications as raw materials, for example, stock materials for rubber materials having chemical and solvent resistance and base components for mold release agents. For example, elastomers can be obtained by reacting a polymer of an organic fluorine compound blocked with an alkenyl group at either end with a compound having at least three hydrosilyl groups in a molecule in the presence of an addition reaction catalyst. These elastomers exhibit high solvent and chemical resistance because of high fluorine contents and are improved in mold release and water repellency because of low surface energy. Then the elastomers are useful as sealants, molded parts, extruded parts, coating materials and mold release agents.

[0033] Also contemplated herein is a curable composition comprising an organic fluorine compound or fluorinated amide compound of formula (1) defined above.

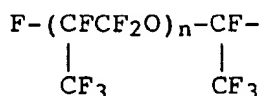
[0034] These curable compositions are now described in detail.

[0035] The curable composition of the invention contains components (A), (B) and (C) as essential components. Component (A) is an organic fluorine compound or fluorinated amide compound of formula (1) defined above. The fluorinated amide compound as component (A) has at least two unsaturated groups in a molecule. In this regard, a fluorinated amide compound of formula (1) wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 10 carbon atoms and said unsaturated group, especially an alkenyl group having 1 to 8 carbon atoms, is used in the curable composition.

[0036] Component (B) of the curable composition is a fluorinated organohydrogensiloxane which serves as a crosslinking agent and chain extender for the fluorinated amide compound (A). The fluorinated organohydrogensiloxane (B) should contain at least one monovalent perfluoroalkyl ether or perfluoroalkyl group and at least two, typically 2 to 50, especially 3 to 20 hydrosilyl (SiH) groups in a molecule. The monovalent perfluoroalkyl ether and perfluoroalkyl groups are preferably those represented by the following general formulae:

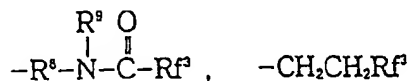


wherein m is an integer of 1 to 10, preferably 2 to 10, and



wherein n is an integer of 1 to 5.

[0037] The fluorinated organohydrogensiloxanes may be of cyclic or chain structure or three-dimensional network. They preferably have at least one monovalent organic group having a perfluoroalkyl or perfluoroalkyl ether group of the following general formula in a molecule as a monovalent substituent attached to a silicon atom.



[0038] In the formulae, R<sup>8</sup> is a divalent hydrocarbon group, preferably having 1 to 6 carbon atoms, for example, alkylene groups such as methylene, ethylene, propylene, methylethylene, tetramethylene, and hexamethylene,

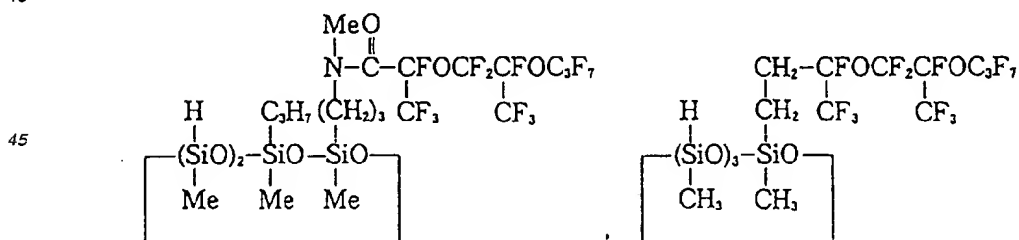
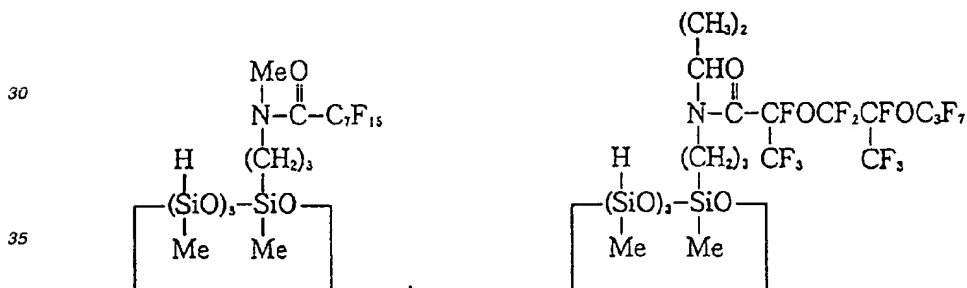
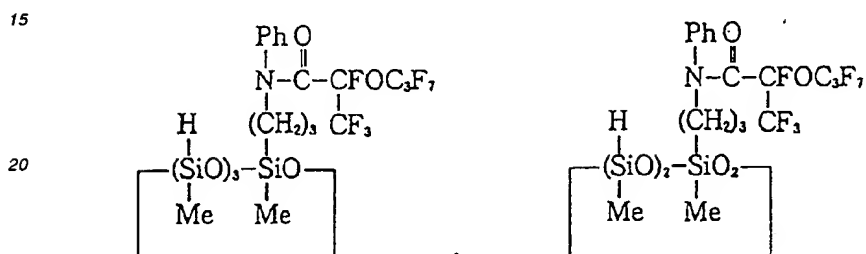
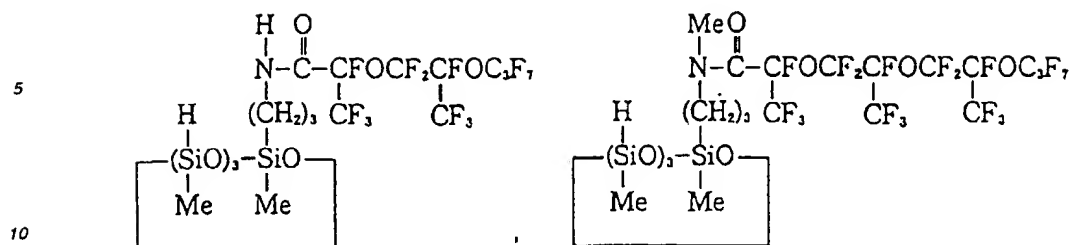
R<sup>9</sup> is a hydrogen atom or a monovalent hydrocarbon group, preferably having 1 to 8 carbon atoms, more preferably 1 to 6 carbon atoms as defined for R<sup>2</sup>, and

R<sup>3</sup> is a monovalent perfluoroalkyl or perfluoroalkyl ether group as previously exemplified.

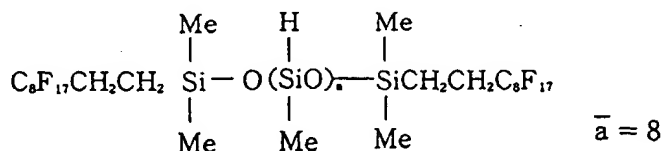
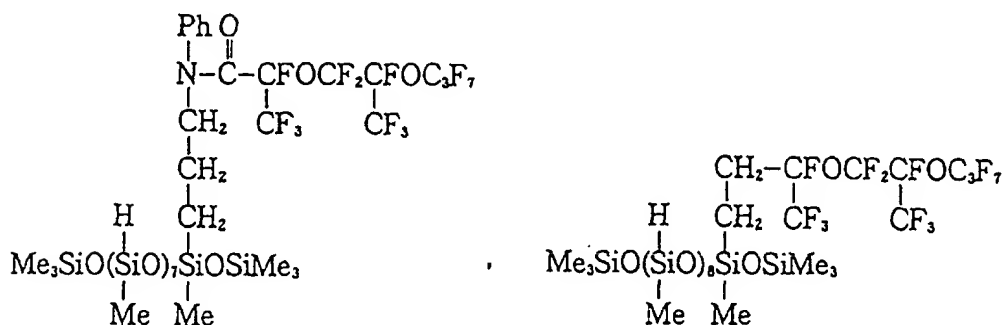
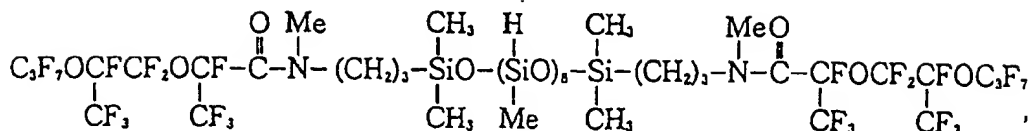
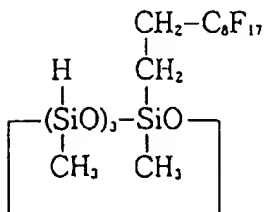
[0039] The fluorinated organohydrogensiloxane (B) has a monovalent substituent group attached to a silicon atom other than the monovalent organic group having a perfluoroalkyl or perfluoroalkyl ether group. Examples of the other substituent group include monovalent hydrocarbon groups free of an aliphatic unsaturated bond, preferably having 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms as previously defined for R<sup>2</sup>.

[0040] The number of silicon atoms per molecule of the fluorinated organohydrogensiloxane is not critical although it generally has about 2 to 50, preferably about 4 to 30 silicon atoms.

[0041] Examples of the fluorinated organohydrogensiloxane are given below. They may be used alone or in admixture of two or more.







**[0042]** When the fluorinated organohydrogensiloxane used as component (B) is compatible with the fluorinated amide compound as component (A), the resulting curable composition will yield a uniform cured product.

**[0043]** Component (B) is berided in the compositon in such an amount as to provide 0.5 to 5 mol, preferably 1 to 2 mol of the hydrosilyl group (i.e., Si-H group) in component (B) per mol of the unsaturated group (e.g., vinyl, allyl and cycloalkenyl groups) in the entire composition, especially component (A). Less than 0.5 mol of the hydrosilyl group on this basis will lead to an insufficient degree of crosslinking. With more than 5 mol of the hydrosilyl group, chain lengthening will become predominant, resulting in short curing or foaming and adversely affecting heat resistance and compression set. Most often, components (A) and (B) are blended such that about 0.1 to 50 parts by weight of component (B) is available per 100 parts by weight of component (A).

**[0044]** The curable composition further contains a platinum group compound as an essential component (C). It is a catalyst for catalyzing addition reaction or hydrosilylation between the fluorinated amide compound and the fluorinated organohydrogensiloxane, that is, serves as a curing promoter. Since the platinum group compounds are generally compounds of noble metals and expensive, relatively easily available platinum compounds are often used.

**[0045]** Illustrative, non-limiting examples of the platinum compound include chloroplatinic acid, complexes of chloroplatinic acid with olefins such as ethylene, complexes of chloroplatinic acid with alcohols or vinylsiloxanes, and platinum on silica, alumina and carbon. Platinum group compounds other than the platinum compounds are also useful. Known examples include compounds of rhodium, ruthenium, iridium, and palladium, for example, such as  $\text{RhCl}(\text{PPh}_3)_3$ .

$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ,  $\text{RhCl}(\text{C}_2\text{H}_4)_2$ ,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , and  $\text{Pd}(\text{PPh}_3)_4$  wherein Ph is phenyl.

[0046] On use, these catalysts may be used in solid form if they are solid catalysts. In order to form more uniform cured products, a solution of chloroplatinic acid or its complex in a suitable solvent is preferably used as a miscible mixture with the fluorinated amide compound (A).

[0047] The amount of the catalyst used is not critical. A desired curing rate will be achieved with a catalytic amount. From an economical point of view or to produce satisfactory cured products, the catalyst is preferably added in an amount of about 1 to 1,000 ppm, more preferably about 10 to 500 ppm of platinum group element based on the weight of the entire curable composition.

[0048] Various additives may be added to any of the curable compositions of the invention in order to enhance their practical usage. Useful additives include polysiloxanes containing a  $\text{CH}_2=\text{CH}(\text{R})\text{SiO}$  unit wherein R is a substituted or unsubstituted monovalent hydrocarbon group (see JP-B 10947/1973) and acetylene compounds (see USP 3,445,420 and JP-B 3774/1979), which are added for the purpose of controlling the curing rate of the curable composition, and ionic compounds of heavy metals (see USP 3,532,649). Where such additives are added, the amount of the fluorinated organohydrogensiloxane blended is determined by taking into account the amount of these additives blended in addition to component (A) or (D). More specifically, 0.5 to 5 mol of Si-H group should be present per mol of the aliphatic unsaturated group (e.g., vinyl, allyl and cycloalkenyl groups) in the entire composition as previously mentioned.

[0049] Moreover, fillers may be blended in the curable compositions of the invention for the purposes of reducing thermal shrinkage upon heating, reducing the coefficient of thermal expansion of elastomers as cured, improving thermal stability, weather resistance, chemical resistance, flame retardancy and mechanical strength, and reducing gas permeability. Exemplary fillers include fumed silica, quartz powder, glass fibers, carbon, metal oxides such as iron oxide, titanium oxide, and cerium oxide, and metal carbonates such as calcium carbonate and magnesium carbonate. If desired, suitable pigments, dyes or anti-oxidants may also be added.

[0050] Any desired method may be used in preparing the curable composition according to the invention. The composition can be prepared simply by kneading the above-defined components. The curable composition as kneaded can be cured at room temperature depending on the type of functional group in the fluorinated amide compound as the first essential component and the type of catalyst as the third essential component. Preferably the composition is cured by heating at 100 to 150°C for several minutes to several hours.

[0051] On use, the curable compositions of the invention may be dissolved in suitable fluorinated solvents such as metaxylene hexafluoride and fluorinert to a desired concentration depending on its application and purpose.

[0052] The curable compositions of the invention may be used in a variety of applications. Cured products resulting from the curable compositions exhibit high solvent and chemical resistance because of high fluorine contents and are improved in mold release and water repellency because of low surface energy. Then the cured products or elastomers are useful as automotive rubber materials required to be oil resistant, tent film materials, sealants, molded parts, extruded parts, coating materials and mold release agents.

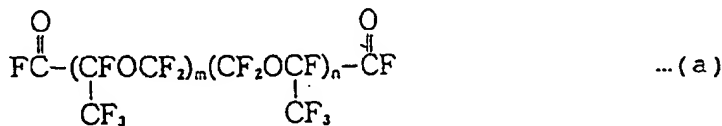
[0053] The preparation methods for the described compositions, methods of use thereof and in particular their use to make any products or articles described above, and the products themselves, are independent aspects of the present invention.

#### EXAMPLE

[0054] Examples of the present invention are given below by way of illustration and not by way of limitation. Note that Me is methyl and Ph is phenyl. All parts are by weight.

#### Example 1

[0055] A 300-ml four-necked flask equipped with a stirrer, thermometer, Dimroth condenser, and dropping funnel was charged with 189.2 g of a compound having an acid fluoride group at each end of the following formula (a) having a viscosity of  $4.3 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (430 centistokes) at 25°C. With stirring, a mixture of 7.1 g of isopropylallylamine and 6.1 g of triethylamine was added dropwise to the flask at 20°C.

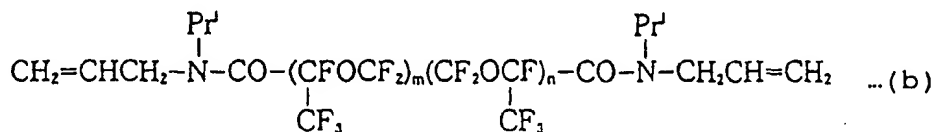


$$\overline{m+n} = 38$$

[0056] After the dropwise addition, reaction was effected at 60°C for 2 hours. The reaction mixture was subject to filtration under pressure and the filtrate was vacuum stripped at 120°C/3 mmHg, yielding 189.5 of a compound as a pale yellow clear liquid. The compound had a viscosity of  $8.41 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (841 centistokes) at 25°C, a specific gravity of 1.832 at 25°C, and a refractive index of 1.3138 at 25°C. The compound was analyzed by IR spectroscopy, with the results shown in FIG. 1. In FIG. 1, the following absorption peaks were observed.

1100-1300 $\text{cm}^{-1}$	$\nu_{\text{C-F}}$
1685 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$

[0057] The allyl content of this compound was quantitatively determined to be 0.031 mol/100 g. From these data, the compound was identified to be a polymer of an organic fluorine compound represented by the following structural formula (b).



[0058]  $\text{Pr}^i$  is isopropyl group.

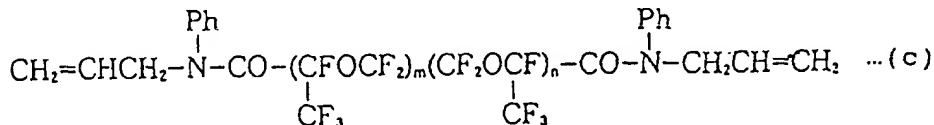
#### Example 2

[0059] A flask as used in Example 1 was charged with 189.2 g of the compound having an acid fluoride group at each end of formula (a) having a viscosity of  $4.30 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (430 centistokes) at 25°C. With stirring, a mixture of 9.6 g of allylaniline and 6.1 g of triethylamine was added dropwise to the flask at 20°C through the dropping funnel. Reaction and post-treatment were done as in Example 1, yielding 190.1 of a compound as a pale yellow clear liquid.

[0060] The compound had a viscosity of  $1.192 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (1192 centistokes) at 25°C, a specific gravity of 1.841 at 25°C, and a refractive index of 1.3208 at 25°C. The compound was analyzed by IR spectroscopy, with the results shown in FIG. 2. In FIG. 2, the following absorption peaks were observed.

1100-1300 $\text{cm}^{-1}$	$\nu_{\text{C-F}}$
1695 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$
1600, 1500 $\text{cm}^{-1}$	arom.

[0061] The allyl content of this compound was quantitatively determined to be 0.031 mol/100 g. From these data, the compound was identified to be a polymer of an organic fluorine compound represented by the following structural formula (c).



[0062] Note that m and n are as in Example 1.

#### Example 3

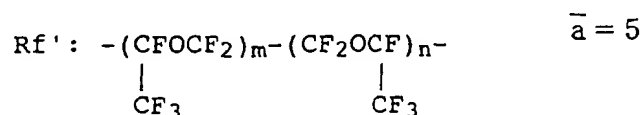
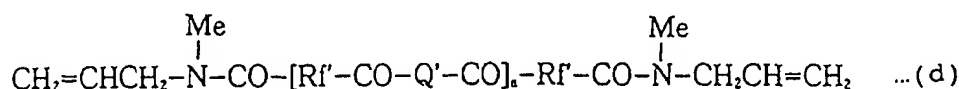
[0063] A 200-ml four-necked flask equipped with a stirrer, thermometer, Dimroth condenser, and dropping funnel was charged with 76.9 g of a compound having an acid fluoride group at each end of formula (a) having a viscosity of  $4.30 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (430 centistokes) at 25°C. With stirring, a mixture of 1.14 g of 2,5-dimethylpiperazine and 2.9 g of triethylamine was added dropwise to the flask at 20°C through the dropping funnel. After the dropwise addition, reaction

was effected at 60°C for 2 hours. After 0.36 g of methylallylamine was added to the reaction mixture, reaction and post-treatment were done as in Example 1, yielding 72.9 g of a compound as a pale yellow clear liquid.

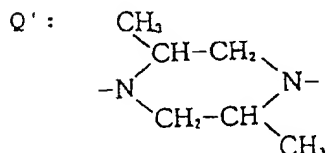
[0064] The compound had a viscosity of  $2.52 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$  (25,200 centistokes) at 25°C. The compound was analyzed by IR spectroscopy, with the results shown in FIG. 3. In FIG. 3, the following absorption peaks were observed.

1100-1300 $\text{cm}^{-1}$	$\nu_{\text{C-F}}$
1690 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$

[0065] The allyl content of this compound was quantitatively determined to be 0.005 mol/100 g. From these data, the compound was identified to be a polymer of an organic fluorine compound represented by the following structural formula (d).

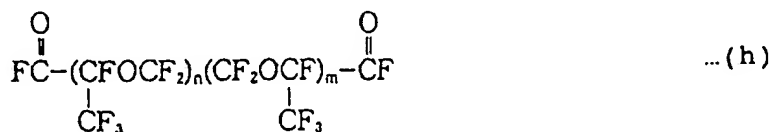


$$m + n = 38$$



#### Example 4

[0066] A flask as used in Example 1 was charged with 200.0 g of a compound having an acid fluoride group at each end of the following formula (h) having a viscosity of  $2.1 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (2,100 centistokes) at 25°C. With stirring, a mixture of 3.6 g of allyl aniline and 2.8 g of triethylamine was added dropwise to the flask through the dropping funnel. Reaction and post-treatment were done as in Example 1, yielding 195.1 g of a compound as a pale yellow clear liquid.



$$\bar{n} + \bar{m} = 107$$

[0067] The compound had a viscosity of  $3.3 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (3,300 centistokes) at 25°C, a specific gravity of 1.883 at 25°C, and a refractive index of 1.309 at 25°C. It was analyzed by IR spectroscopy, with the results shown in FIG. 4. In FIG. 4, the following absorption peaks were observed.

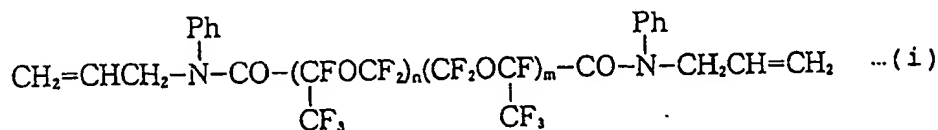
1100-1300 $\text{cm}^{-1}$	$\nu_{\text{C-F}}$
1705 $\text{cm}^{-1}$	$\nu_{\text{C=O}}$

(continued)

1600, 1500 cm<sup>-1</sup>

arom.

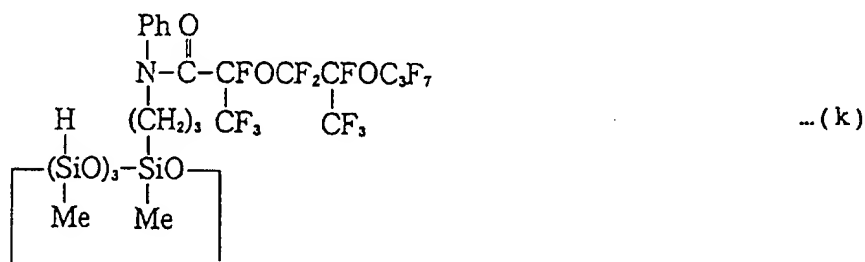
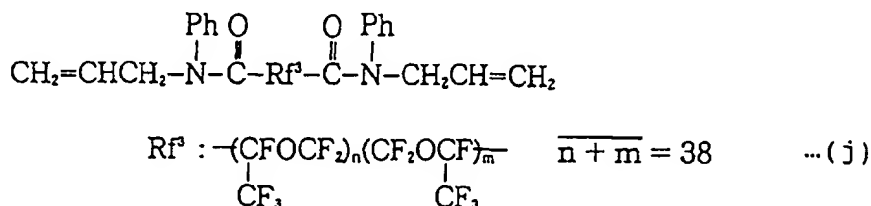
[0068] The compound was quantitatively determined to find an allyl content of 0.011 mol/100 g. From these data, the compound was identified to be a polymer of an organic fluorine compound having the following structural formula (i).



[0069] Note that m and n are as defined above.

#### Example 5

[0070] To 100 parts of a polymer of the following formula (j) having a viscosity of  $1.19 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  (1,190 centistokes) at 25°C, an average molecular weight of 7,000 and an allyl content of 0.029 mol/100 g was added 10 parts of fumed silica having a specific surface area of 200 m<sup>2</sup>/g and treated with trimethylsiloxy group. They were mixed, heat treated, and milled on a three-roll mill. To the compound were further added 10.8 parts of a fluorinated cyclohydrogensiloxane of the following formula (k) and 0.2 part of a toluene solution of a chloroplatinic acid catalyst modified with  $\text{CH}_2=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2$  (platinum concentration 1.0% by weight), with mixing continued.



[0071] The resulting composition was defoamed under vacuum, placed in a rectangular frame of 2 mm high, deaerated again, and press cured at 120 kg/cm<sup>2</sup> and 150°C for 20 minutes. A specimen was cut from the cured sheet and measured for physical properties according to JIS K-6301, with the results shown below.

Hardness (JIS-A)	43
Elongation (%)	180
Tensile strength (kgf/cm <sup>2</sup> )	25

Note that hardness in JIS A scale was measured using a type A spring hardness tester prescribed in JIS K-6301.

[0072] The specimen was also examined for heat resistance, solvent swell, chemical resistance, and low-temperature properties. The results are shown in Tables 1 to 4.

# EP 0 688 762 B1

Table 1:

Heat resistance				
		Initial	3 days	7 days
5	150°C			
	Hardness (JIS-A)	43	58 (+15)	55 (-12)
	Elongation (%)	180	160 (-48)	90 (-73)
10	TS (kgf/cm <sup>2</sup> )	25	20 (-13)	27 (-63)
	Heat loss (%)	-	0	0.3
	200°C			
	Hardness (JIS-A)	43	60 (+17)	35 (-12)
15	Elongation (%)	180	90 (-73)	80 (-78)
	TS (kgf/cm <sup>2</sup> )	25	26 (-76)	24 (-76)
	Heat loss (%)	-	0.6	0.8
Note: Figures in parentheses are percents based on the initial, but increase or decrease of points for hardness.				

Table 2:

Solvent swell	
Solvent	Volume change (%)
FuelC	+16
FuelC/methanol = 75/25	+19
FuelC/methanol = 50/50	+16
FuelC/methanol = 25/75	+10
Methanol	+1
Chloroform	+21
Acetone	+14
Toluene	+11
Isopropyl alcohol	+2
Acetonitrile	+3
Methyl ethyl ketone	+17
Ethyl acetate	+19
Tetrahydrofuran	+23
n-hexane	+14
Carbon tetrachloride	+21
FuelC: a mixture of toluene and isooctane in a volume ratio of 50/50	

Table 3:

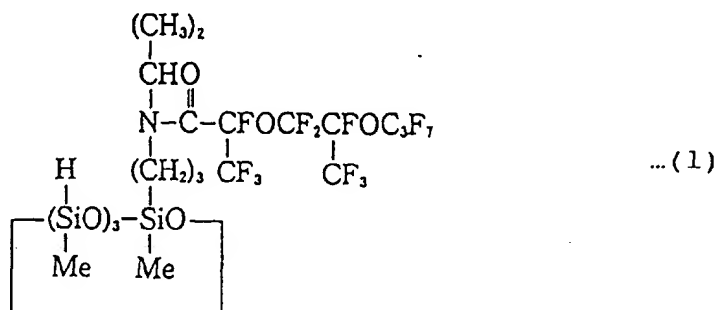
Chemical resistance (change of rubber hardness)		
	Hardness	Surface state
Initial	43	-
conc. hydrochloric acid	55 (+12)	no change
conc. sulfuric acid	38 (-5)	deteriorated
40% potassium hydroxide	40 (-3)	no change
Note: Figures in parentheses are increase or decrease of points.		
Deterioration conditions: 20°C/3 days		

Table 4:

Low-temperature property (German twist test)	
$T_2$	-20°C
$T_5$	-31°C
$T_{10}$	-38°C
$T_{100}$	-48°C

Example 6

[0073] A composition was prepared by the same procedure as in Example 5 except that 10.6 parts of a fluorinated cyclohydrogensiloxane of the following formula (1) was used instead of the fluorinated cyclohydrogensiloxane of formula (k). A cured sheet was similarly prepared therefrom.

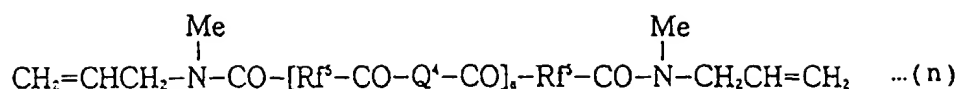


[0074] A specimen cut from the cured sheet was similarly measured for physical properties, with the results shown below.

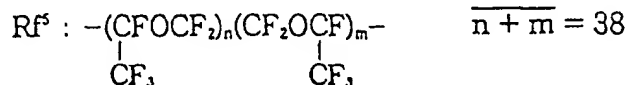
Hardness (JIS-A)	40
Elongation (%)	200
Tensile strength (kgf/cm <sup>2</sup> )	22

Example 7

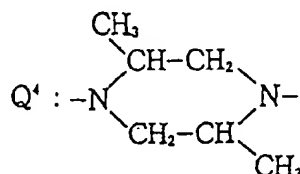
[0075] A composition was prepared by the same procedure as in Example 5 except that 100 parts of a polymer of the following formula (n) having a viscosity of  $1.31 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$  (13,100 centistokes) at 25°C, an average molecular weight of 19,200 and an allyl content of 0.010 mol/100 g was used instead of the polymer of formula (j) and 3.5 parts of the fluorinated cyclohydrogensiloxane in Example 5 was used. A cured sheet was similarly prepared therefrom.



$$\overline{a} = 4$$



$$\overline{n} + \overline{m} = 38$$

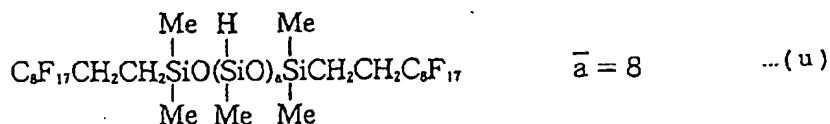
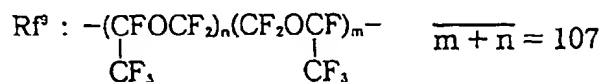


[0076] A specimen cut from the cured sheet was similarly measured for physical properties, with the results shown below.

Hardness (JIS-A)	45
Elongation (%)	280
Tensile strength (kgf/cm <sup>2</sup> )	53

#### Example 8

[0077] A composition was prepared by the same procedure as in Example 5 except that 100 parts of a polymer of the following formula (t) having a viscosity of  $3.3 \times 10^{-3} \text{m}^2 \text{s}^{-1}$  (3,300 centistokes) at 25°C, an average molecular weight of 18,100 and an allyl content of 0.011 mol/100 g was used instead of the polymer of formula (j) and 3.1 parts of a fluorinated cyclohdrogensiloxane of the following formula (u) was used instead of the fluorinated cyclohdrogensiloxane in Example 5. A cured sheet was similarly prepared therefrom.



[0078] A specimen cut from the cured sheet was similarly measured for physical properties, with the results shown below.

Hardness (JIS-A)	46
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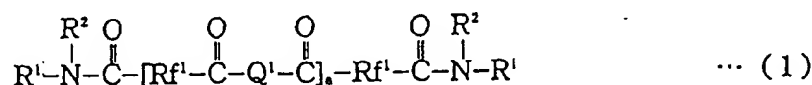
(continued)

Elongation (%)	200
Tensile strength (kgf/cm <sup>2</sup> )	23

[0079] Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the claims the invention may be practised otherwise than as specifically described in the Examples.

## Claims

1. An organic fluorine compound of the following general formula (1):



wherein

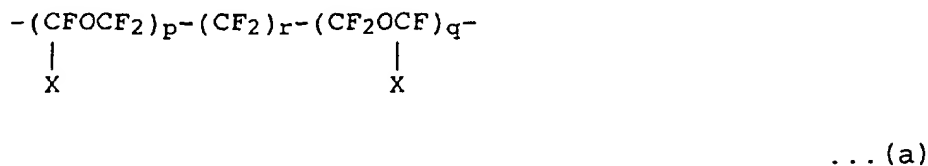
R<sup>2</sup> groups are selected from halogen-substituted and unsubstituted monovalent hydrocarbon groups;  
 R<sup>1</sup> groups are selected from halogen-substituted and unsubstituted monovalent C<sub>2-10</sub> alkenyl, cycloalkenyl or alkenyl-substituted aryl groups;  
 Q<sup>1</sup> is a group selected from groups of the following general formula (3):



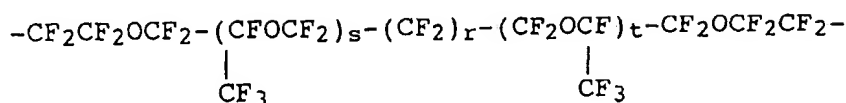
wherein

R<sup>4</sup> and R<sup>5</sup> are independently selected from halogen-substituted and unsubstituted divalent hydrocarbon groups;  
 Rf<sup>1</sup> is a divalent perfluoroalkylene or perfluoropolyether group, and  
 a is an integer which may be 0.

2. An organic fluorine compound according to claim 1 in which R<sup>2</sup> groups are selected from C<sub>1-10</sub> alkyl, C<sub>2-10</sub> alkenyl, aryl and aralkyl hydrocarbon groups, optionally with halogen substitution, and R<sup>1</sup> groups are selected from vinyl, allyl, propenyl, isopropenyl, butenyl, isobutenyl, hexenyl, cyclohexenyl and styryl.
3. An organic fluorine compound according to claim 1 or 2 in which a is non-zero and, for formula (3), R<sup>4</sup> and R<sup>5</sup> are independently selected from C<sub>1-10</sub> alkylene and cycloalkylene up to C<sub>10</sub>, optionally with halogen substitution.
4. An organic fluorine compound according to any one of the preceding claims in which Rf<sup>1</sup> is selected from perfluoroalkylene groups of the formula -C<sub>m</sub>F<sub>2m</sub>- where m = 1 to 10, and perfluoropolyether groups according with any of the formulae (a) to (d) below:

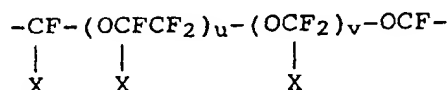


wherein X is F or CF<sub>3</sub> group, p, q and r are integers satisfying: p ≥ 1, q ≥ 1, and 2 ≤ p + q ≤ 200, especially 3 ≤ p + q ≤ 110 and 0 ≤ r ≤ 6,



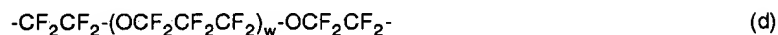
... (b)

wherein r, s and t are integers satisfying: 0 ≤ r ≤ 6, s ≥ 0, t ≥ 0, and 2 ≤ s + t ≤ 200, especially 3 ≤ s + r ≤ 110,



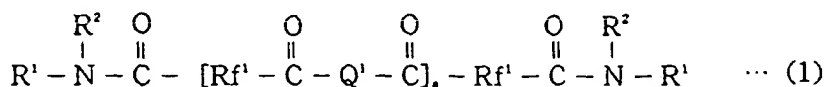
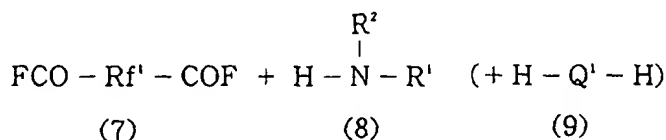
... (c)

wherein X is F or CF<sub>3</sub> group and u and v are integers satisfying: 1 ≤ u ≤ 20 and 1 ≤ v ≤ 20, and



wherein w is an integer in the range 1 ≤ w ≤ 20.

5. An organic fluorine compound according to any one of the preceding claims in the form of a raw rubber-like polymer composition having a viscosity in the range 1×10<sup>-4</sup> to 1×10<sup>-1</sup>m<sup>2</sup>s<sup>-1</sup> (100 to 100,000 cs) at 25°C.
6. A method of making an organic fluorine compound according to any one of the preceding claims comprising reacting an acid fluoride-terminated compound of formula (7) with a secondary amine compound of formula (8), and optionally as appropriate with a compound of formula (9), in the presence of an acid acceptor as follows:



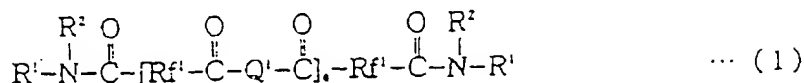
7. A curable composition comprising

- (A) organic fluorine compound according to any one of claims 1 to 5;
- (B) fluorinated organohydrogensiloxane containing per molecule at least one monovalent perfluoroalkyl ether or perfluoroalkyl group and at least two hydrosilyl groups, and
- (C) a catalytic amount of platinum group catalyst; component (B) being present in an amount to give from 0.5 to 5 mole hydrosilyl group to mole of unsaturated group.

8. An elastomeric article made by curing a composition according to claim 7.

# Patentansprüche

1. Organische Fluorverbindung der folgenden allgemeinen Formel (1):



worin

die R<sup>2</sup>-Gruppen aus Halogen-substituierten und unsubstituierten einwertigen Kohlenwasserstoffgruppen ausgewählt sind;  
 die R<sup>1</sup>-Gruppen aus Halogen-substituierten und unsubstituierten einwertigen C<sub>2-10</sub>-Alkenyl-, Cycloalkenyl- oder Alkenyl-substituierten Arylgruppen ausgewählt sind;  
 Q<sup>1</sup> eine Gruppe ist, die aus Gruppen der folgenden allgemeinen Formel (3) ausgewählt ist:



worin

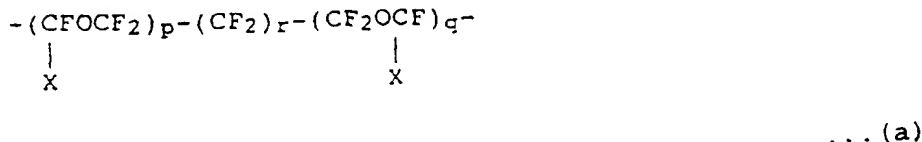
R<sup>4</sup> und R<sup>5</sup> unabhängig voneinander aus Halogen-substituierten und unsubstituierten zweiwertigen Kohlenwasserstoffgruppen ausgewählt sind;  
 R<sup>1</sup> eine zweiwertige Perfluoralkylen- oder Perfluorpolyethergruppe ist, und  
 a eine ganze Zahl ist, die 0 sein kann.

2. Organische Fluorverbindung nach Anspruch 1, bei der die R<sup>2</sup>-Gruppen aus C<sub>1-10</sub>-Alkyl-, C<sub>2-10</sub>-Alkenyl-, Aryl- und Aralkylkohlenwasserstoffgruppen, gegebenenfalls mit Halogen-Substitution, ausgewählt sind, und die R<sup>1</sup>-Gruppen aus Vinyl, Allyl, Propenyl, Isopropenyl, Butenyl, Isobutenyl, Hexenyl, Cyclohexenyl und Styryl ausgewählt sind.

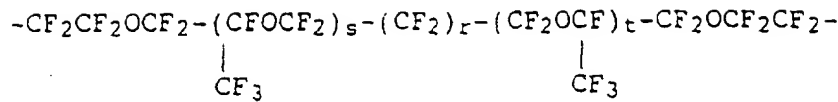
3. Organische Fluorverbindung nach Anspruch 1 oder 2, in der a ≠ 0 ist und für Formel (3) R<sup>4</sup> und R<sup>5</sup> unabhängig voneinander aus C<sub>1-10</sub>-Alkenyl und Cycloalkenyl bis zu C<sub>10</sub>, gegebenenfalls mit Halogen-Substitution, ausgewählt sind.

4. Organische Fluorverbindung nach einem der vorangegangenen Ansprüche, in der R<sup>1</sup> aus

Perfluoralkylengruppen der Formel -C<sub>m</sub>F<sub>2m</sub>-, worin m = 1 bis 10 ist, und  
 Perfluorpolyethergruppen nach einer der nachstehenden Formeln (a) bis (d) ausgewählt ist:

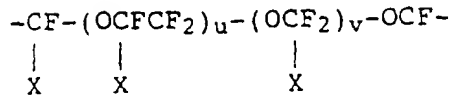


worin X = F oder eine CF<sub>3</sub>-Gruppe ist, p, q und r ganze Zahlen sind, für die gilt: p ≥ 1, q ≥ 1 und 2 ≤ p + q ≤ 200, insbesondere 3 ≤ p+q ≤ 110 und 0 ≤ r ≤ 6,



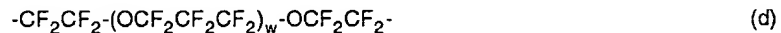
... (b)

worin r, s und t ganze Zahlen sind, für die gilt:  $0 \leq r \leq 6$ ,  $s \geq 0$ ,  $t \geq 0$  und  $2 \leq s+t \leq 200$ , insbesondere  $3 \leq s+r \leq 110$ ,



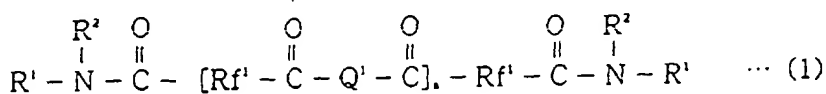
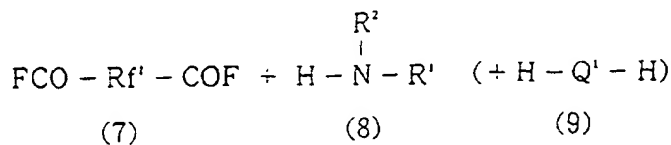
... (c)

worin X = F oder eine CF<sub>3</sub>-Gruppe ist und u und v ganze Zahlen sind, für die gilt:  $1 \leq u \leq 20$  und  $1 \leq v \leq 20$ , und



worin w eine ganze Zahl im Bereich  $1 \leq w \leq 20$  ist.

5. Organische Fluorverbindung nach einem der vorangegangenen Ansprüche in Form einer rohkautschukartigen Polymerzusammensetzung mit einer Viskosität bei 25 °C im Bereich von  $1 \times 10^{-4}$  bis  $1 \times 10^{-1} \text{ m}^2\text{s}^{-1}$  (100 bis 100.000 cSt).
6. Verfahren zur Herstellung einer organischen Fluorverbindung nach einem der vorangegangenen Ansprüche, umfassend das Umsetzen einer Verbindung mit Säurefluorid-Endgruppen der Formel (7) mit einer sekundären Aminverbindung der Formel (8), und nach Bedarf gegebenenfalls mit einer Verbindung der Formel (9), in Gegenwart eines Säurefängers wie folgt:



7. Härtbare Zusammensetzung, umfassend:

- (A) eine organische Fluorverbindung nach einem der Ansprüche 1 bis 5;  
 (B) fluoriertes Organohydrogensiloxan, das pro Molekül zumindest eine einwertige Perfluoralkylether- oder Perfluoralkylgruppe und zumindest zwei Hydrosilylgruppen enthält, und  
 (C) eine katalytische Menge an Platingruppenkatalysator;

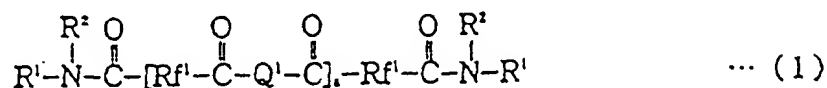
wobei Komponente (B) in einer Menge vorhanden ist, die 0,5 bis 5 Mol Hydrosilylgruppen pro Mol an unge-

sättigten Gruppen ergibt.

8. Elastomer-Gegenstand, hergestellt durch Härtung einer Zusammensetzung nach Anspruch 7.

# Revendications

1. Composé de fluorure de la formule générale (1) qui suit:



où

les groupes  $\text{R}^2$  sont sélectionnés parmi des groupes hydrocarbures monovalents, halogénosubstitués et non substitués;

les groupes  $\text{R}^1$  sont sélectionnés parmi des groupes aryle, alcényle, cycloalcényle ou alkaryle substitués  $\text{C}_{2-10}$  monovalents halogénosubstitués et non substitués;

$\text{Q}^1$  est un groupe sélectionné dans les groupes de la formule générale (3) qui suit:



où

$\text{R}^4$  et  $\text{R}^5$  sont indépendamment sélectionnés parmi des groupes hydrocarbures divalents halogénosubstitués et non substitués;

$\text{Rf}^1$  est un groupe perfluoroalkylène ou perfluoropolyéther divalent, et

$a$  est un entier qui peut être 0.

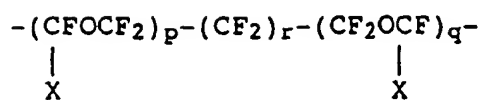
2. Composé de fluor organique selon la revendication 1 où les groupes  $\text{R}^2$  sont sélectionnés parmi des groupes hydrocarbures alkyle  $\text{C}_{1-10}$ , alcényle  $\text{C}_{2-10}$ , aryle et aralkyle, facultativement avec substitution halogène et les groupes  $\text{R}^1$  sont sélectionnés parmi vinyle, allyle, propényle, isopropényle, butényle, isobutényle, hexényle, cyclohexényle et styryle.

3. Composé de fluor organique selon la revendication 1 ou 2 où  $a$  est non-zéro et, pour la formule (3),  $\text{R}^4$  et  $\text{R}^5$  sont indépendamment sélectionnés parmi alkylène  $\text{C}_{1-10}$  et cycloalkylène jusqu'à  $\text{C}_{10}$ , facultativement avec substitution halogène.

4. Composé de fluor organique selon l'une quelconque des revendications précédentes dans lequel  $\text{Rf}^1$  est sélectionné parmi

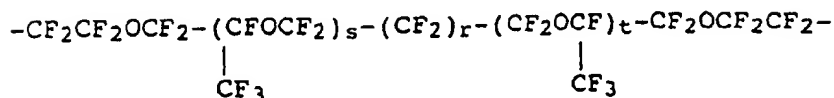
groupes perfluoroalkylène de la formule  $-\text{C}_m\text{F}_{2m}-$  où  $m = 1$  à 10, et

groupes perfluoropolyéther selon l'une quelconque des formules (a) à (d) ci-dessous:



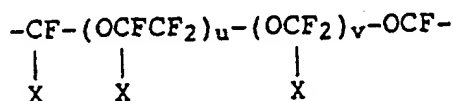
... (a)

où X est F ou un groupe CF<sub>3</sub>, p, q et r sont des entiers satisfaisant: p ≥ 1, q ≥ 1, et 2 ≤ p + q ≤ 200, en particulier 3 ≤ p + q ≤ 110 et 0 ≤ r ≤ 6,



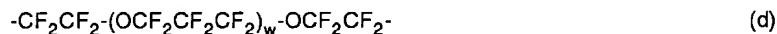
... (b)

où r, s et t sont des entiers satisfaisant: 0 ≤ r ≤ 6, s ≥ 0, t ≥ 0, et 2 ≤ s + t ≤ 200, en particulier 3 ≤ s + r < 110,



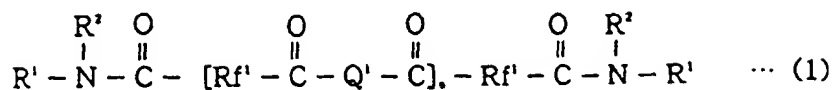
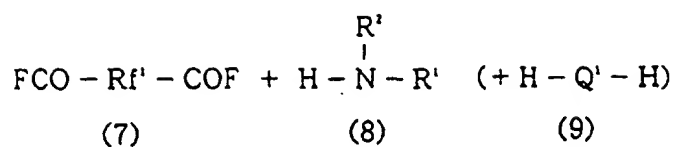
... (c)

où X est F ou un groupe CF<sub>3</sub> et u et v sont des entiers satisfaisant: 1 ≤ u ≤ 20 et 1 ≤ v ≤ 20, et



où w est un entier dans la gamme de 1 ≤ w < 20.

5. Composé de fluor organique selon l'une quelconque des revendications précédentes sous la forme d'une composition d'un polymère ressemblant à du caoutchouc brut ayant une viscosité dans la gamme de 1 x 10<sup>-4</sup> à 1 x 10<sup>-1</sup> m<sup>2</sup>s<sup>-1</sup> (100 à 100 000 cs) à 25°C.
6. Méthode de production d'un composé de fluor organique selon l'une quelconque des revendications précédentes comprenant la réaction d'un composé terminé en fluorure d'acide de formule (7) avec un composé d'amine secondaire de formule (8), et facultativement, selon ce qui est approprié, avec un composé de formule (9), en présence d'un accepteur d'acide comme suit:

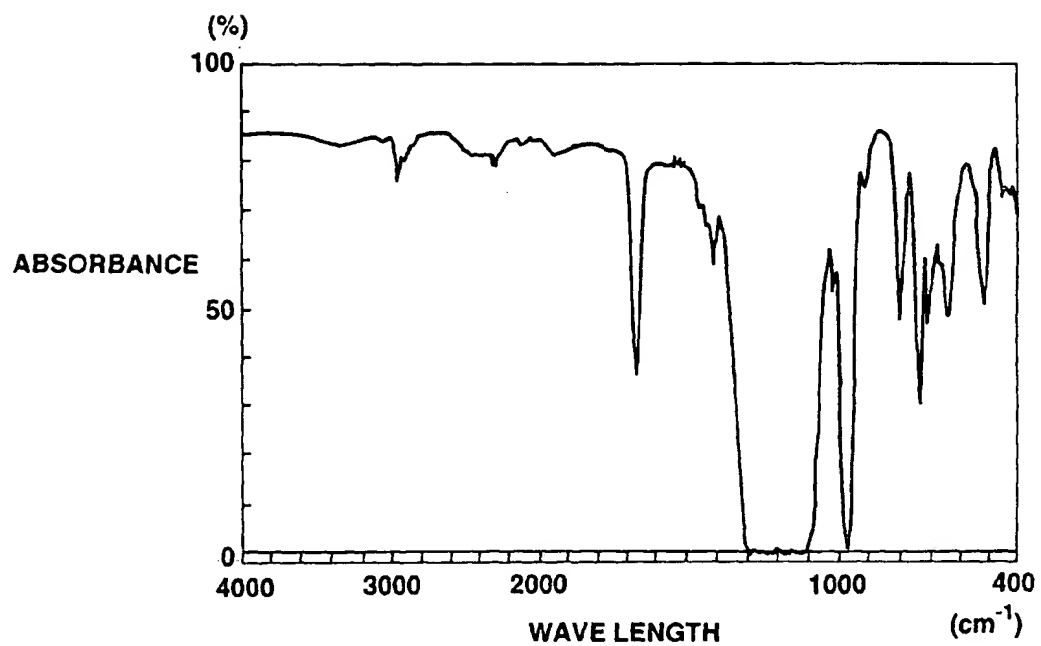


# 7. Composition durcissable comprenant

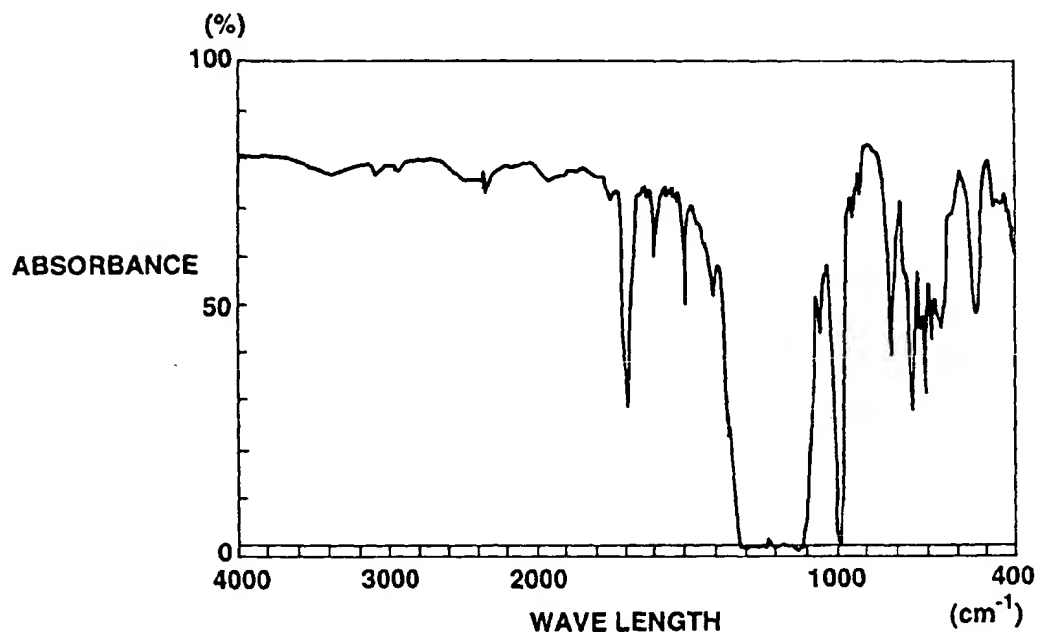
- (A) un composé de fluor organique selon l'une quelconque des revendications 1 à 5,  
 (B) un organohydrogénosiloxane fluoré contenant par molécule au moins un groupe perfluoroalkyle ou perfluoroalkyl éther monovalent et au moins deux groupes hydrosilyle, et  
 (C) une quantité catalytique d'un catalyseur du groupe platine; le composant (B) étant présent en une quantité pour donner de 0,5 à 5 moles du groupe hydrosilyle par mole du groupe insaturé.

# 8. Article élastomère fait en durcissant une composition selon la revendication 7.

**FIG.1**

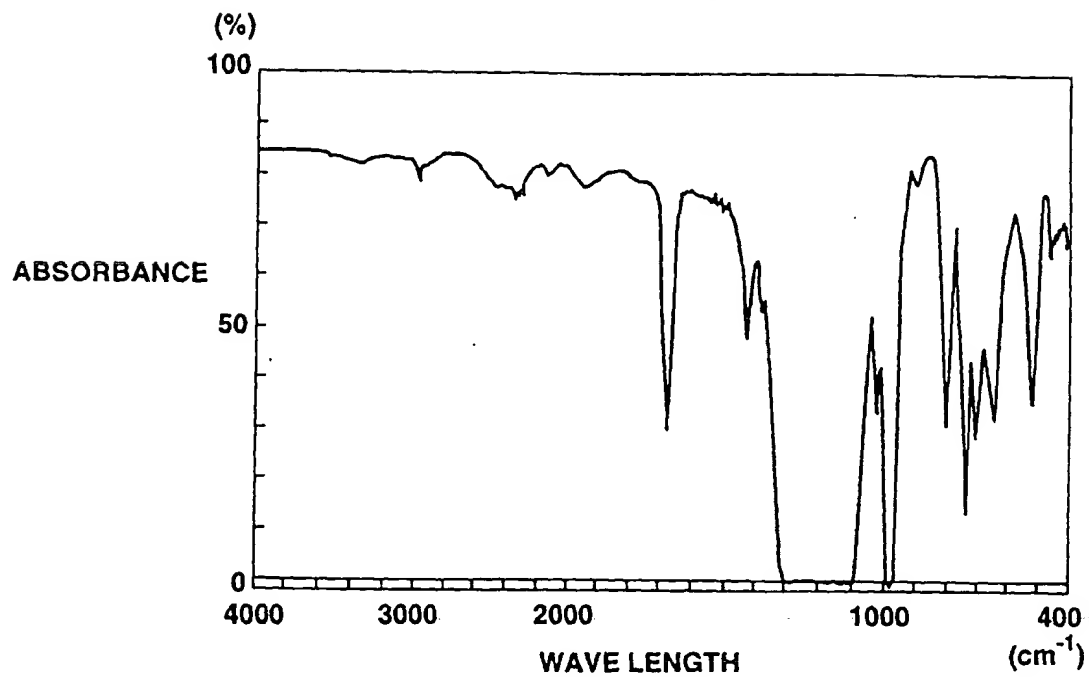


**FIR.2**





**FIG.3**



**FIG.4**

